



## Research paper

## Aqueous-phase reforming of methanol over nickel-based catalysts for hydrogen production



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## ARTICLE INFO

## Article history:

Received 27 May 2017

Received in revised form

7 August 2017

Accepted 11 August 2017

## Keywords:

Aqueous-phase reforming

Methanol

Hydrogen

Nickel-based catalyst

Biorefinery

## ABSTRACT

Water fractions derived from biofuel production contain oxygenated hydrocarbons that can be converted by aqueous-phase reforming (APR) into hydrogen. As a result, the product efficiency of biorefineries may improve. However, the hydrothermal and high pressure operating conditions of APR limit the reaction kinetics, thermodynamics and catalyst stability. To overcome these limitations, an active and durable catalyst should be developed to selectively convert oxygenated hydrocarbons into hydrogen. For this study, methanol was selected as a model compound. Nickel-based catalysts with dopants such as copper and cerium and different supports were tested for the APR of methanol. The results revealed enhanced performance of doped catalysts in comparison to monometallic materials, and the effect of supports improved in the order  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> <  $\beta$ -SiC < ZrO<sub>2</sub> <  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Accordingly, NiCe/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> exhibited the highest values of methanol conversion and hydrogen yield. These results satisfied the target of this study to develop an active and hydrogen-selective catalyst and proved the suitability of cerium-doped nickel on alumina to convert methanol into hydrogen.

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## 1. Introduction

Biofuels can be produced from lignocellulosic biomass and waste streams of biomass processing [1]. Lignocellulosic biomass can be processed for instance by gasification to produce syngas or by fast pyrolysis to produce bio-oil [2,3]. Upgrading of syngas or bio-oil to biofuels involves the production of waste water fractions with oxygenated hydrocarbons that are considered as environmental pollutants [4,5]. Oxygenated hydrocarbons can be converted into hydrogen by aqueous-phase reforming (APR) [6,7] to minimize the disposal of organic waters. Hydrogen can be further utilized to process syngas in a Fischer-Tropsch (FT) unit or for bio-oil hydrotreatment. As a result, the efficiency of biofuel production processes can be improved.

Organic waters derived from biorefineries constitute a complex mixture of oxygenated hydrocarbons challenging to process. Therefore, model compounds are frequently used as feedstock to

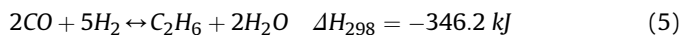
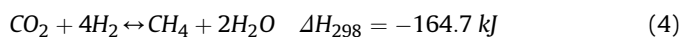
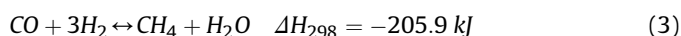
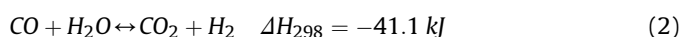
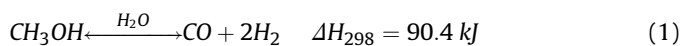
study APR. Glycerol [8–10] is commonly selected to represent the water fraction derived from the production of biodiesel. Ethylene glycol [11–13] is highly considered because it represents a by-product of the APR of glycerol. Sorbitol and xylitol [14], methanol and ethanol [15], acetic acid [16] and real mixtures derived from biomass processing [17] are additionally regarded. The operating conditions of APR at low temperatures (200 °C–250 °C) and moderate pressures (1.5 MPa–5.0 MPa) [18] avoid an energy-consuming evaporation step. Accordingly, APR is a promising route to produce hydrogen because it is an energetically efficient process [19]. The efficiency is particularly evident when a highly diluted feedstock is considered. Furthermore, low temperatures thermodynamically facilitate the production of low-CO hydrogen. However, at these operating conditions, the thermodynamics also favours undesired side reactions to form hydrocarbons and carbohydrates. The kinetics of the main reactions is additionally limited due to low temperature and mass transfer limitations [20]. Aiming at increasing hydrogen yield and selectivity, the effect of reaction conditions and the performance of different catalysts have been widely investigated [7]. APR is commonly catalysed by platinum and nickel-based catalysts [21–25]. Platinum supported on

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alumina reaches high conversions and hydrogen selectivity [26–28], whereas nickel-based catalysts constitute an economically attractive alternative with lower stability and hydrogen selectivity [29–31]. Ni has been doped with metals including Cu, Ce and Sn [32–34], and supported on different metal oxides and carbonaceous materials [35–37] to improve hydrogen yield and catalyst stability.

The water fractions derived from the conversion of lignocellulosic biomass to biofuels have received slight consideration as APR feedstock. The number of studies on the APR of methanol and other model compounds found in those waters is scarce. Published research on the APR of methanol over nickel-based catalyst is limited to Ni Sn-Raney [20]. Methanol was selected as a model compound for this study because it is one of the compounds in higher concentration in the water fractions derived from both FT process and fast pyrolysis bio-oil refining [38,39]. In the APR of methanol, hydrogen is produced through C-H and/or O-H bond cleavage (Eqs. (1) and (2)). Moreover, methane and ethane can be formed by hydrogenation of carbon oxides after C-O bond scission (Eqs. (3)–(5)). Accordingly, a suitable catalyst for hydrogen production should promote the reactions specified in Eqs. (1) and (2), and inhibit the reactions in Eqs. (3)–(5).



To find an active nickel-based catalyst for the APR of methanol to selectively produce hydrogen is the intended outcome of this study. For that purpose, nickel and nickel promoted with copper and cerium were supported on  $\beta$ -SiC,  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$ . In addition, due to the broad application and high performance of Pt/ $\gamma$ - $\text{Al}_2\text{O}_3$ , this catalyst was selected as a benchmark catalyst. This work gives insights into the performance of nickel-based catalyst in APR for hydrogen production to potentially optimize the production of biofuels.

## 2. Experimental

### 2.1. Catalysts

Nickel and bimetallic combinations of nickel and copper or cerium supported on porous silicon carbide and metal oxides, and Pt/ $\gamma$ - $\text{Al}_2\text{O}_3$  were tested in aqueous-phase reforming of methanol. Ni/ $\alpha$ - $\text{Al}_2\text{O}_3$  catalyst was supplied by BASF, SICAT supplied  $\beta$ -SiC, and Saint Gobain Norpro and Engelhard supplied  $\gamma$ - $\text{Al}_2\text{O}_3$ . Zirconium hydroxide was supplied by MEL Chemicals in amorphous form, which was calcined at 600 °C in air to obtain  $\text{ZrO}_2$  support. The supports were first crushed and sieved to a particle size of (200–300)  $\mu\text{m}$ . Thereafter, the metals were loaded by wet or incipient wetness impregnation methods (Table 1). Nickel ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\geq 97.0\%$ ), copper ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , 99%–104%) and cerium ( $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\geq 99.0\%$ ) nitrates were the metal precursors supplied by Sigma-Aldrich.

For the wet impregnation (WI in Table 1), either Ni-precursor or Ni- and Cu- or Ce-precursors were dissolved in 50  $\text{cm}^3$  of distilled water. The support was added to the solution and stirred for 24 h at room temperature. Subsequently, the water was evaporated at

110 °C under vacuum. The resulting catalyst was calcined at 450 °C for 2.5 h in flowing nitrogen. To prepare the catalysts by incipient wetness impregnation (IWI in Table 1), the supports were dried and afterwards impregnated with solutions of Ni-precursor, or simultaneously with Ni-, and Cu- or Ce-precursors. After drying, the catalysts were calcined at 500 °C for 2 h in flowing air.

### 2.2. Catalyst characterization

The metal content of fresh catalysts was determined by atomic absorption spectroscopy (AAS) and/or X-ray fluorescence (XRF). The AAS analyses were conducted for the catalyst supported on  $\beta$ -SiC. Samples of 0.2 g were first dissolved in  $\text{HNO}_3$  and HCl at 120 °C to determine the Ni and Cu content. After the samples cooled down, these were diluted with Milli-Q water. A Varian AA240 AAS device was applied to measure the nickel and copper content using air-acetylene flame. X-Ray fluorescence (XRF) measurements were performed in a wavelength dispersive PANalytical AXIOSmax analyzer with a SST-mas X-Ray source. XRF analyses were conducted to determine the metal content in all the alumina and zirconia-supported catalysts, and the cerium content in the  $\beta$ -SiC-supported catalyst.

The surface properties of pure supports and fresh catalysts were determined from nitrogen physisorption data. The adsorption and desorption isotherms were obtained by a Micromeritics Tristar 3000 device. Prior to the physisorption, catalyst samples of approximately 0.5 g were degassed overnight at 300 °C under helium flow. The BET method was used to calculate the surface area. Pore volume and diameter were calculated by the BJH method with data from the desorption-isotherm.

Surface species were determined by X-ray diffraction (XRD) in a PANalytical X'Pert PRO MPD Alpha-1 diffractometer with Cu  $K\alpha 1$  radiation (45 kV and 40 mA). The X-ray scanning was performed in continuous scan mode in the range 10°–90° (2 $\theta$ ) and a step size of 0.0131°. In addition, the crystallite diameter of nickel was estimated using the Scherrer equation based on the peak broadening of the most intense NiO peak of fresh catalysts.

### 2.3. Catalytic activity tests

The performance of the catalysts listed in Table 1 was tested for aqueous-phase reforming of methanol (MeOH) in a laboratory-scale system (Fig. 1). The catalysts (1.5 g) were loaded in the midsection of a continuously operated tubular stainless steel reactor with 12 mm of inner diameter. The catalysts were reduced in-situ for one hour with a 1:1 mixture of  $\text{H}_2$  and  $\text{N}_2$  at atmospheric pressure, and temperature specified in Table 1. Aqueous-phase reforming was conducted at 230 °C and 3.2 MPa. A methanol solution with a mass fraction of 5% was pumped by a HPLC pump (Fig. 1, GA-1) and fed upwards into the reactor (Fig. 1, DC-1) with a weight hourly space velocity (WHSV, calculated as grams of methanol per hour divided by grams of catalyst) of 2  $\text{h}^{-1}$ . Downstream the reactor, nitrogen was fed to strip the products and as an internal standard to determine the production rate of gaseous products. The outlet stream was thereupon cooled down (Fig. 1, HE-1) and separated into gas and liquid phases (Fig. 1, HD-1) at the operating pressure.

The outlet streams were sampled every 20 min for approximately 3 h. The gaseous and liquid products were analysed online and offline respectively by gas chromatography (GC). The gases were analysed in a HP5890 Series II gas chromatograph equipped with TCD (Thermal Conductivity Detector) and FID (Flame Ionization Detector), and a Carboxen 1000 column. An Agilent technologies 7890A GC System equipped with a FID and a HP-INNOWax Polyethylene Glycol column was used to analyse the liquid

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